



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification³ : C04B 7/35, 7/54, 13/22	A1	(11) International Publication Number: WO 84/ 02900 (43) International Publication Date: 2 August 1984 (02.08.84)
(21) International Application Number: PCT/SE84/00011 (22) International Filing Date: 17 January 1984 (17.01.84) (31) Priority Application Number: 8300283-2 (32) Priority Date: 20 January 1983 (20.01.83) (33) Priority Country: SE (71) Applicant (for all designated States except US): CEMENTA AB [SE/SE]; Box 144, S-182 12 Danderyd (SE). (72) Inventor; and (75) Inventor/Applicant (for US only) : NORELIUS, Per [SE/SE]; Herscrudsvägen 9 D, S-181 34 Lidingö (SE). (74) Agents: HJÄRNE, Per-Urban et al.; H Albihns Patentbyrå AB, Box 7664, S-103 94 Stockholm (SE).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), NO, RO, SE (European patent), SU, US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: A METHOD OF REDUCING ECZEMA-INDUCING CHROMIUM IN CEMENT BY ADDING FERROUS SULFATE, AN ADDITIVE COMPRISING FERROUS SULFATE AND THE USE OF THE ADDITIVE (57) Abstract <p>In order to reduce the risk of chromium eczema when working with cement, the hexavalent chromium in the cement is reduced with ferrous sulfate in the form of ferrogypsum. Ferrogypsum is prepared by mixing green salt, a waste product from i.a. the manufacture of titanium dioxide, in moist state without any preceding drying or granulating, with gypsum in predetermined proportions. The ferrogypsum is used in making cement as a replacement for the ordinary gypsum and is added to the cement milling process with the existing dosing system for the gypsum. In order to reduce the content of easily soluble, hexavalent chromium from ca 10 ppm to ca 0.5 ppm, an addition of green salt is required of ca 5-10 kg per ton of cement. With a normal gypsum addition of 50 kg per ton of cement, the ferrogypsum should consist of 10% by weight green salt and 90% by weight gypsum and be added in an amount of 52 kg per ton of cement.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	KR	Republic of Korea
AU	Australia	LI	Liechtenstein
BE	Belgium	LK	Sri Lanka
BG	Bulgaria	LU	Luxembourg
BR	Brazil	MC	Monaco
CF	Central African Republic	MG	Madagascar
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SD	Sudan
FR	France	SE	Sweden
GA	Gabon	SN	Senegal
GB	United Kingdom	SU	Soviet Union
HU	Hungary	TD	Chad
JP	Japan	TG	Togo
KP	Democratic People's Republic of Korea	US	United States of America

A method of reducing eczema-inducing chromium in cement by adding ferrous sulfate, an additive comprising ferrous sulfate and the use of the additive.

Portland cement always contains a certain amount of readily soluble hexavalent chromium in the form of chromates, usually 10-20 ppm Cr^{6+} , stemming from the raw material and in smaller amounts from the fuel, the kiln lining and the various machines. This chromium produces eczema in bricklayers and concrete workers among others. A known and tested additive for reducing the content of easily soluble hexavalent chromium in the concrete, and thus reducing the risk of chromium contact eczema, is divalent iron in the form of ferrous sulfate.

Ferrous sulfate is present in large amounts in the form of so-called green salt, a waste product from certain chemical and hydrometallurgical process industries. When extracting titanium dioxide from ilmenite with sulphuric acid leaching, 3-4 tons of green salt are obtained for example for each ton of titanium dioxide. A small amount of this can be used for water purification, but the major portion is deposited as waste or is pumped into the sea.

Green salt is such ferrous sulfate which leaves a precipitation process after a varying degree of mechanical dehydration by filtering and possibly centrifuging. The major component of the green salt is ferrous sulfate with 7 hygroscopic water, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, with varying amounts of impurities and a moisture content of 2-25 % by weight depending on the dehydration method. Centrifuged green salt has the consistency of wet snow.

Green salt has been approved as a concrete additive and is sold in 25 kg plastic bags for manual addition in conjunction with the mixing of concrete.

Up to now, for adding ferrous sulfate to cement during mixing, there has been necessary to use dry ferrous sulfate in



the form of granulates or powder, produced from the green salt in special drying or granulating plants. Such purified ferrous sulfate can be easily stored, transported and dosed by means of known technology and can also be easily mixed with the dry cement powder. In addition to being substantially more expensive than the corresponding amount of green salt, it is also dusty and moisture sensitive and therefore requires sealed handling with special equipment for freight, storage and internal transport in bulk form, or alternatively the use of the product in sacks, which makes the product even more expensive. Such dry ferrous sulfate is at present being used in a Danish cement plant.

It is primarily three factors which prevent the ready addition of green salt to the cement mixer. In the first place, it is not possible to store, transport and dose green salt with sufficient reliability in a mechanized, remote controlled and automated continuous process in the same manner as can be done with dry ferrous sulfate. In the second place, green salt can have a negative effect on the grinding process itself by hardened deposits in the mill with tendencies for blockage especially at the mill inlet. In the third place, an excessively high water content of the ferrous sulfate can cause the chromate-reducing effect to be lost when the green salt with an excess of water is subjected in the cement mill to an alkaline environment and high temperature.

When using green salt for water purification for example, the handling problem can be avoided by dumping the salt directly into a tank for dissolving and then add the ferrous sulfate solution to the process. A corresponding technique has also been tried in the cement industry by spraying a saturated aqueous solution of the green salt into the cement mill, but this produced insufficient chromate reduction in the concrete. Another method which has been tested is to pump into the mill a slurry consisting



of undissolved ferrous sulfate and saturated ferrous sulfate solution, but this process did not produce sufficient chromate reduction either.

- 5 The present invention intends to produce cement with an additive of green salt in a mechanized and automated process with already existing equipment, by a method which does not produce the negative effects on the cement mill operation and which produces sufficient chromate reduction to
10 eliminate the risk of eczema.

Cement refers here to all hydraulic binders and mortar products containing Portland cement clinker as the major component, 1-10 % by weight gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as a regulator
15 of setting time and varying amounts of additives such as limestone, ash, slag and silicon powder, e.g. an amorphous, finely dispersed kieselguhr from the manufacture of silicon, ferrosilicon and ferrochromium.

- 20 Green salt refers to a wet to moist salt containing 15-20 % iron in the form of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 2-25 % by weight of non-chemically bonded water.

The invention is based on replacing the ordinary gypsum
25 component in the cement milling with a mixture of gypsum and green salt, called ferrogypsum in the following, which is responsible in the process both for controlling the setting time and chromate reduction.

- 30 This premixture of gypsum and green salt is possible by virtue of the fact that these substances are chemically closely related and tests have shown that the mixture has good resistance when stored against oxidation of the divalent iron.

35

The gypsum can be natural gypsum or so-called chemical gypsum, a by-product of certain chemical processes,



especially the production of phosphoric acid. The granules of chemical gypsum are normally fine and can be easily mixed with green salt into a homogeneous mixture which will not separate during handling up to the cement mill. When
5 using natural gypsum, one should select a quality with a low proportion of heavy particles over about 20 mm, so that the separation of gypsum and green salt will be minimized.

The composition of the ferrogypsum must be such that the
10 amount of sulfate which regulates the setting time and the amount of divalent iron for reducing chromates have a certain relative proportion in view of the desired sulfate content in the finished cement, the original content of easily soluble chromate and the desired chromate reduction.
15 The sulfate content and the chromate content in the cement vary from case to case, but have been shown to be virtually constant over time for a particular production unit. It is therefore possible to maintain the composition of the ferro-gypsum once it has been determined.

20 A suitable addition of ferrous sulfate is 3-12 kg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per ton of finished cement, depending on the original content of Cr^{6+} in the cement clinker and the desired chromate reduction. In order to keep the sulfate content in the
25 cement for regulating the setting time unchanged, the addition of gypsum is reduced by 0.6 parts gypsum for each part ferrous sulfate heptahydrate added.

In order to reduce the content of Cr^{6+} from 10 ppm to 0.5
30 ppm, ca 5 kg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are required per ton of cement. If 50 kg of gypsum were originally added per ton of cement, this must then be reduced by 0.6x5 kg to 47 kg. The ferro-gypsum can in this case consist of about 10 % by weight green salt and 90 % by weight gypsum and be added to the
35 cement grinding process in an amount corresponding to 47+5= 52 kg per ton cement. The mixing proportions of green salt and gypsum can be adjusted somewhat in view of the prevailing moisture and impurity contents in the raw materials.



If the original content of easily soluble hexavalent chromium in the cement is higher than 10 ppm or if it is desired to make an even greater chromate reduction, the proportion of green salt in the ferrogypsum is raised to
5 at most about 20 kg per ton of cement.

The proportion of green salt in the ferrogypsum can also be reduced if the original content of Cr^{6+} in the cement is lower than 10 ppm or if the chromate reduction is not
10 to be carried as far. In the same manner, the mixing in of green salt in the ferrogypsum can be calculated from the size of the gypsum addition if it is initially greater or less than 50 kg per ton of cement. The proportion of green
15 salt in the ferrogypsum can then vary from case to case between 2 and 90 % by weight, preferably between 5 and 25 % by weight.

As is previously mentioned, the ferrogypsum has good storage stability and the cement grinding process is rela-
20 tively insensitive to fluctuations in the composition of the ferrogypsum, due to inhomogeneity. This allows the ferrogypsum to be prepared with simple equipment and at the most advantageous location for transport, for example at the factory or delivery location for gypsum or green
25 salt, at the reloading terminal or at the cement factory.

The preparation of the ferrogypsum can be done by laying out a specific quantity of gypsum on a flat supporting surface in a layer about one meter thick. On top of this
30 there is then laid a layer of a certain amount of green salt corresponding to the desired mixing proportions. The materials can be laid out with a bucket loader and the mixture can be homogenized by redigging with the loader, whereafter the mixture is loaded into a bin for transport
35 to the next station, which can be a ship or a transport vehicle, intermediate storage plant or dosing bin for feeding into a cement mill.



The ferrogypsum thus produced can then be used as a replacement for gypsum in the making of cement after recalculating the dosing as specified above.

5 In full scale tests at the cement plant in Degerhamn, 100 tons of ferrogypsum were prepared by mixing 10 tons of green salt containing 10 % moisture with 90 tons of chemical gypsum, whereafter the mixture was stored for one month prior to addition to the cement mill. The dosing corresponded to 6 kg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per ton of cement and the content of easily soluble, hexavalent chromium in the cement was reduced from the original 12 ppm to an average of 0.6 ppm. The storage stability of the ferrogypsum is thus very good and completely sufficient to continue a cement production where the storage time is at most a few weeks. Additional full scale tests were done at the cement plant in Skövde with three different mixtures containing 9 %, 12.5 % and 16.7 %, respectively, of green salt with ca 5 % moisture in the gypsum, which corresponded to 4.5 kg, 6.5 kg and 8.5 kg, respectively, of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per ton of cement. The amount of easily soluble Cr^{6+} was reduced from the original 11 ppm to 1.2 ppm, 1.0 ppm and 0.55 ppm, respectively. The chromium contents refer to analyses done after two minutes of shaking of equal amounts of cement and water.

25 Storage tests have been made with finished cement which immediately after the manufacture had 0.25 ppm easily soluble chromium. The chromium content remained unchanged for two months and after three months it had risen to 0.5 ppm and after seven months to 0.7 ppm.

During the tests, the ferrogypsum had better handling properties than both green salt and gypsum individually due to less dust and easy passage through loading bins and shuts.

35 The special features of this invention compared with already known products and processes for addition of ferrous sulfate



and gypsum are the following:

The invention provides a method for using green salt as a chromate reducing raw material because

- 5 - the ferrogypsum has significantly better handling characteristics than green salt, and at least equally good handling characteristics as gypsum;
- the ferrogypsum does not negatively affect the operation of the cement mill with baked-on deposits and the like,
10 as is the case when using green salt and gypsum individually;
- the divalent iron in the ferrogypsum is only oxidated to an insignificant degree to trivalent iron during the
15 milling process, which can be done by direct addition of wet green salt and gypsum individually.

The invention permits the replacement of two additives by a single additive which provides appreciable advantages as regards transport and economy. No extra investments are
20 required for the addition of ferrous sulfate in each production line, as is the case with separate addition of ferrous sulfate and gypsum. Rather, existing equipment is used.

By virtue of the fact that the common dosing will assure
25 that the total weight of gypsum and green salt is constant, the fluctuations in sulfate content in the cement which would otherwise arise due to uneven dosing of ferrous sulfate are largely eliminated. The dosing of the ferrous sulfate thus does not need to be as exact as when the
30 ferrous sulfate and gypsum are added separately to the cement mill.

It is also possible to centralize the mixing of ferrogypsum to a location from which it can be distributed to a number
35 of cement plants, thus profiting from the economies of scale over separate handling of ferrous sulfate and gypsum. The mixing can be done on a larger scale, water transport can be



done in fewer and larger boats, and the existing receiving and storage system for gypsum at the cement plant can be used.

- 5 The present invention thus provides a simple method for producing a cement with significantly reduced risk of chromium eczema, without changing existing production lines, by using an inexpensive waste product, and the finished cement has equally good properties as cement
10 without the addition, and at the same time without risk of causing chromium eczema.

15



CLAIMS

1. Method of reducing eczema-inducing chromium in cement by adding ferrous sulfate, characterized in that ferrous sulfate in the form of green salt without previous drying is mixed with calcium sulfate in the form of natural gypsum or chemical gypsum into a ferrogypsum with a content of ferrous sulfate heptahydrate of 2-90 % by weight and a content of calcium sulfate dihydrate of 10-98 % by weight and is added to the starting materials included in the finished cement in amounts corresponding to 10-100 kg per ton of cement.
2. Method according to Claim 1, characterized in that the ferrogypsum is added in the milling process.
3. Ferrogypsum for making cement with a low content of eczema-inducing chromium in water and concrete, characterized in that it consists of a physical mixture of ferrous sulfate in the form of raw green salt which has not been pre-dried and calcium sulfate in the form of natural gypsum or chemical gypsum, the proportion of ferrous sulfate heptahydrate being 2-90 % by weight and the proportion of calcium sulfate dihydrate 10-98 % by weight.
4. Ferrogypsum according to Claim 5, characterized in that the content of ferrous sulfate heptahydrate is 5-25 % by weight and the content of calcium sulfate dihydrate 75-95 % by weight.
5. The use of ferrogypsum according to any one of Claim 3 or 4 as an additive in the manufacture of cement with a low content of eczema-inducing, easily soluble chromium in mortar and concrete.



INTERNATIONAL SEARCH REPORT

International Application No PCT/SE84/00011

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC 3		
C 04 B 7/35, 7/54, 13/22		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC 2,3	C 04 B 7/24, 7/35, 7/36, 7/38, 7/52, 7/54, 11/12, 13/22; C 01 G 49/14	
US C1	106:89, 100-103, 314; 423: 588	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched *		
SE, NO, DK, FI classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT 14		
Category *	Citation of Document, 15 with Indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
X	US, A, 3 425 892 (MR EDELSON ET AL) 4 February 1969, see in particular col.1, lines 54-57, col.3, lines 1-14, example 1.	1-5
X	EP, A, 54 314 (AKTIESELSKABET AALBORG PORTLAND-CEMENT-FABRIK) 23 June 1982, see in particular p.1, lines 32-33, p.2, lines 1-13	1-5
A	Chemical Abstracts, Vol.79 (1973), abstract No. 96214c, Acta Derum - Venereol, 1973, 53 (4), 267-270.	
A	Chemical Abstracts, Vol.88 (1978) abstract No. 140777a, Nordisk Betong, 1977, 6, 28-30.	
A	US, A, 2 307 270 (W W HODGE) 4 August 1940	
E,X	WO, A, 84/01942 (AKTIESELSKABET AALBORG PORTLAND-CEMENT-FABRIK) 24 May 1984	1-5
<p>* Special categories of cited documents: 16</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report 2	
1984-06-20	1984-06-20	
International Searching Authority *	Signature of Authorized Officer 19	
Swedish Patent Office	Eva Ahlén	

K.L.